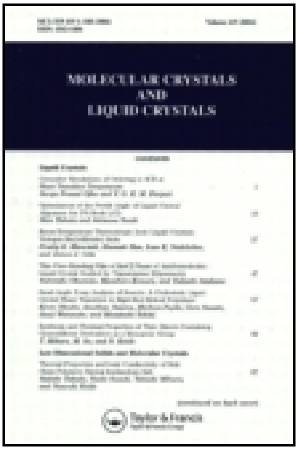

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NEW OPTICAL MEMORY EFFECTS IN POLYMER-STABILIZED CHOLESTERIC LIQUID CRYSTALS DUE TO PITCH CHANGES DURING THE UV-CURING

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NEW OPTICAL MEMORY EFFECTS IN POLYMER-STABILIZED CHOLESTERIC LIQUID CRYSTALS DUE TO PITCH CHANGES DURING THE UV-CURING

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A Polymer-Stabilized Cholesteric Liquid Crystal (PSCLC) is elaborated by combining the UV-curing with a thermally-induced pitch variation. We intend investigating possible memory effects into the characteristics of the reflection band of the PSCLC when the material comes back to the room temperature. Different thermal processes are studied when the curing occurs at one or two temperatures (with the role of the inverse sequence for the latter case). In the visible spectrum, the reflection bandwidth can be tuned in agreement with the chosen process and broadened by several orders of magnitude. The PSCLCs are switchable: broadened reflective, scattering and transparent states are the main modes occurring when a cell is subjected to an increasing voltage. Related application fields are smart windows for the control of solar light spectrum and white-or-black polarizer-free reflective displays.

Keywords: Bragg light reflection; broadband reflection; polymer-stabilized cholesteric liquid crystals; reflective displays

I. INTRODUCTION

The spatially twisted structure of the cholesteric liquid crystal (CLC) phase gives rise to remarkable physical properties [1]. The most symbolic optical property is probably the strong selective Bragg reflection exhibited by a CLC slab with a uniformly oriented Grandjean planar texture [2]. At normal incidence, the mean reflection wavelength $\bar{\lambda}$ is related to the cholesteric

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pitch p and the mean refraction index $\bar{n}$ [3] by:

$$\bar{\lambda} = \bar{n}\,p.$$

The reflection occurs in a wavelength bandwidth $\Delta\lambda$:

$$\Delta\lambda = p\ \Delta n$$

where Δn is the birefringence [4].

Within $\Delta\lambda$, an incident unpolarized or linearly polarized light beam parallel to the helix axis is split into two opposite circularly polarized components, one of which is transmitted whereas the other is totally reflected. The sense of rotation of the latter one agrees with the helix screw sense. A wavelength out of $\Delta\lambda$ is simply transmitted. Since Δn values are limited for colourless organic compounds, $\Delta\lambda$ is often less than 100 nm in the visible spectrum.

Polymer-Stabilized LCs (PSLCs) or anisotropic gels are composite materials made of a crosslinked LC polymer and nonreactive low molar mass LCs (LMMLCs) such as cyanobiphenyl mixtures [5]. These materials are produced by the *in situ* UV-polymerization of LC monomers in the presence of the LC solvent. The polymer content is a few weight percent. Depending on the pitch range, PSCLCs exhibit specific optical and electro-optical properties which give rise to bistable reflective displays or light shutters with normal and reverse modes [6].

Here we report a novel route to elaborate PSCLCs which combines the UV-curing with a thermally-induced pitch variation (what we have called out-of-equilibrium conditions). We intend investigating possible memory effects into the characteristics of the reflection band of the PSCLC when the material comes back to the room temperature. Different thermal processes are studied depending on the curing occurs at one or two temperatures (with the role of the inverse sequence for the latter case).

II. EXPERIMENTAL CONDITIONS

A photocrosslinkable CLC, RM9 (from Wacker Chemie Ltd.), is blended with a LMMLC. RM9 is a mesomorphic oligomer suited for the production of optical filters and consists of a mixture of reactive monomers and side groups LC polymers with a siloxane backbone [7]. An amount of 2 wt.% (compared to RM9 concentration) of photoinitiator Irgacure 907 (from Ciba-Geigy) is added. The LMMLC is a blend of BL087, BL088 and CB15 mixtures from Merck Ltd. The concentration (in wt.%) is as follows: 70x[82xBL088 + 18xCB15] + 30xBL087. In the final blend, the concentration in network-forming material (RM9) is 3.85 wt.%.

The blend is introduced at room temperature by capillarity in a 15 μm (±3 μm) thick ITO-glass cell (from EHC CO. Ltd., type FF). In order to induce a planar orientation the surfaces were treated with rubbed polyimide (rubbing direction: 180°).

The sample is cured with UV-light at 365 nm with a power of 0.1 mW.cm^{-2} (measured with a UV-radiometer UVR-365 from Prolabo) during 30 minutes.

The transmitted light intensity as a function of wavelength is investigated by unpolarized spectrophotometry (UV-3100 Shimadzu) at room temperature. It is checked that negative peaks are due to reflectance and not to absorbance. As usually, $\bar{\lambda}$ and $\Delta\lambda$ are measured from the spectrum by considering respectively the wavelength for the minimum of transmitted light inside the peak and the peak bandwidth at half-height.

During the study of electro-optical properties, the voltage is a square-wave signal and the frequency is equal to 500 Hz.

III. RESULTS

III.1. Polymorphism of the CLC Blend Before Curing

The blend presents a cholesteric phase at room temperature. Grandjean planar textures were investigated by polarized-light microscopy between crossed polarizers when the temperature is increased from 22°C until the cholesteric-isotropic transition which begins at 72°C (biphasic texture). Inside this range the reflection colour varies from orange to dark red as shown in Figure 1. Three temperatures have been chosen as marks for the different thermal processes: 35, 52 and 67°C.

The pitch variation with the temperature has been investigated by using the Grandjean–Cano wedge method [8]. As displayed in Figure 2, the pitch varies from 420 to 528 nm when the temperature varies from 22 to 67°C. At 35, 52 and 67°C, the pitch is equal to respectively 438, 472 and 528 nm.

III.2. One-step Process: UV-Curing at A Single Temperature

Figure 3 shows the variation of transmitted intensity as a function of the wavelength for cells before and after curing at three reference temperatures. Prior curing, $\bar{\lambda}$ is around 620–630 nm. Although shifted towards smaller values, $\bar{\lambda}$ is kept rather constant whatever the curing temperature is. Prior curing, $\Delta\lambda$ is about 86–89 nm. $\Delta\lambda$ was not significantly modified when the curing occurred at the lowest temperatures (35 and 52°C). On the other hand, the curing at 67°C gave rise to a broadening of the wavelength bandwidth: $\Delta\lambda$ is now equal to 190 nm which means an increase of about 120% (*i. e.* $\Delta\lambda$ has been multiplied by 2.2).

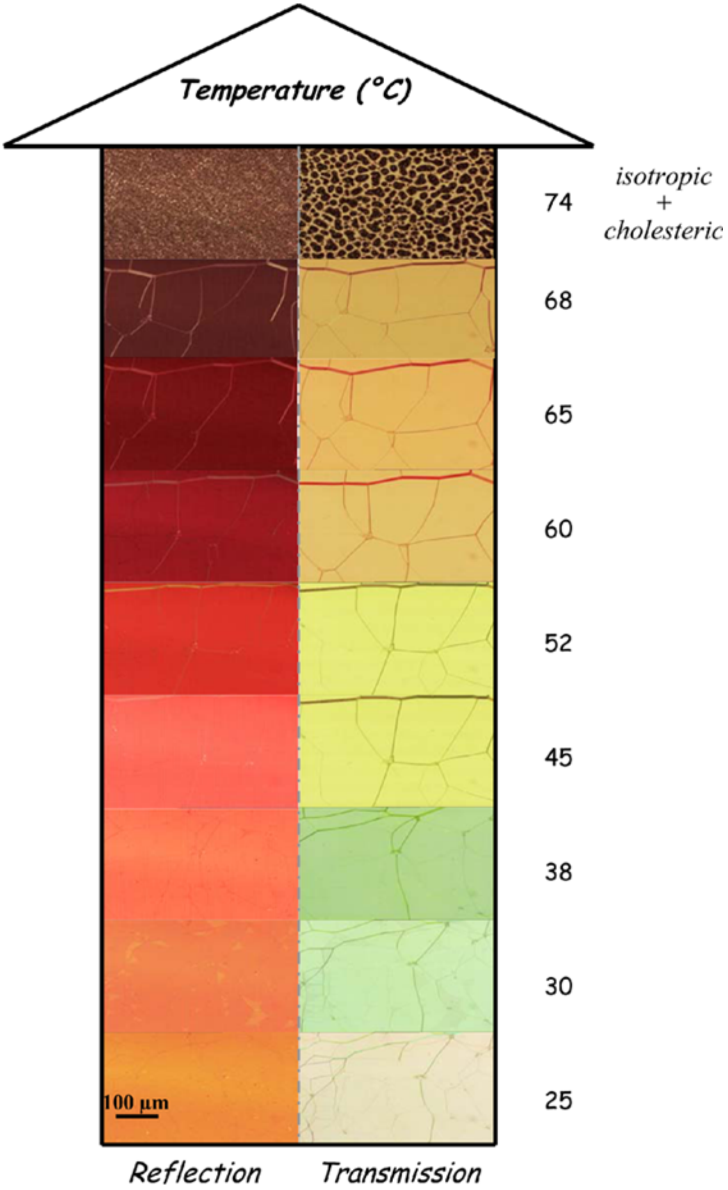

FIGURE 1 - Polymorphism of the CLC blend before curing: optical textures at different temperatures (crossed polarizers). (See COLOR PLATE XXXII)

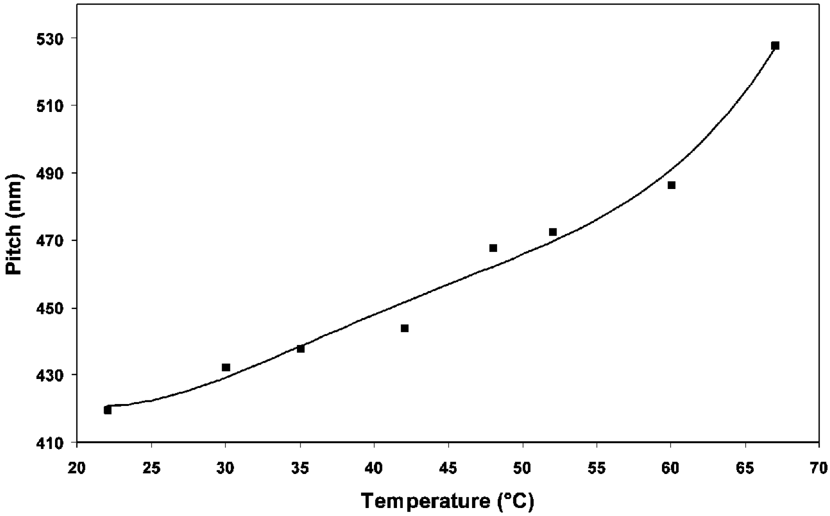

FIGURE 2 Helical pitch of the CLC blend before curing as a function of temperature.

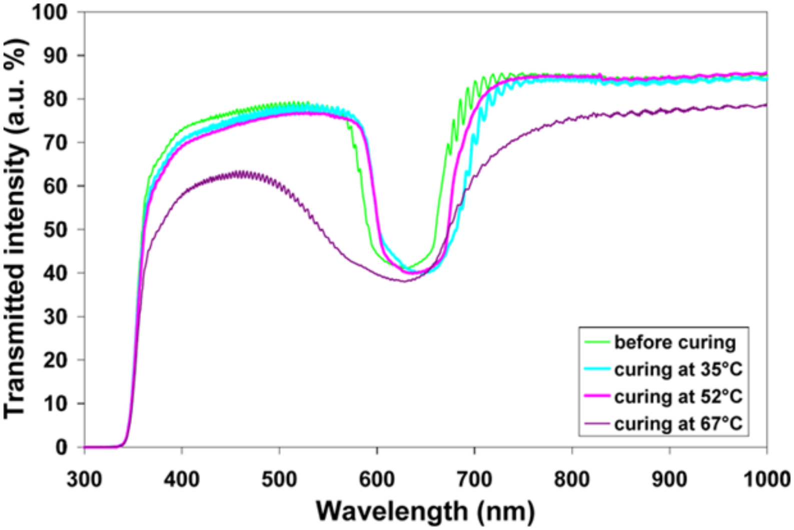

FIGURE 3 Transmitted light intensity of cells as a function of wavelength before and after UV-curing at three different temperatures. (See COLOR PLATE XXXIII)

III.3. Two-step Process: UV-Curing at Two Successive Temperatures

Figure 4 shows the variation of transmitted intensity with the wavelength when one and the same cell is cured at two temperatures, 67 and then 35°C. For each temperature the irradiation time was equal to 15 minutes. After curing, the peak is enlarged by about 165% ($\Delta\lambda \sim 223\,\text{nm}$) by comparison with $\Delta\lambda$ assigned to the peak before curing.

In summary, we investigated the reflection properties of PSCLCs when elaborated during the following sequences: 35 & 52°C, 52 & 67°C, 35 & 67°C and the inverse sequences (*i.e.* from high to low temperature). Whatever the sequence be, the peak position stays rather constant: the $\bar{\lambda}/\bar{\lambda}_0$ ratio ($\bar{\lambda}_0$ and $\bar{\lambda}$ are the mean reflection wavelengthes before and after curing) varies from 96.0 to 100.5%. However $\Delta\lambda$ is significantly changing. Figure 5 displays the $\Delta\lambda$ values for PSCLCs prepared during the above-quoted thermal processes. Figure 5a corresponds to the processes from low to high temperature and Figure 5b describes the inverse sequences. Figure 5a shows that $\Delta\lambda$ varies from 97 to 186 nm; within this set of conditions the more important $\Delta\lambda$ values are obtained when 67°C belongs to the sequence. In Figure 5b, $\Delta\lambda$ varies from 90 to 223 nm. For all the processes presented here, the highest $\Delta\lambda$ values are obtained when the curing

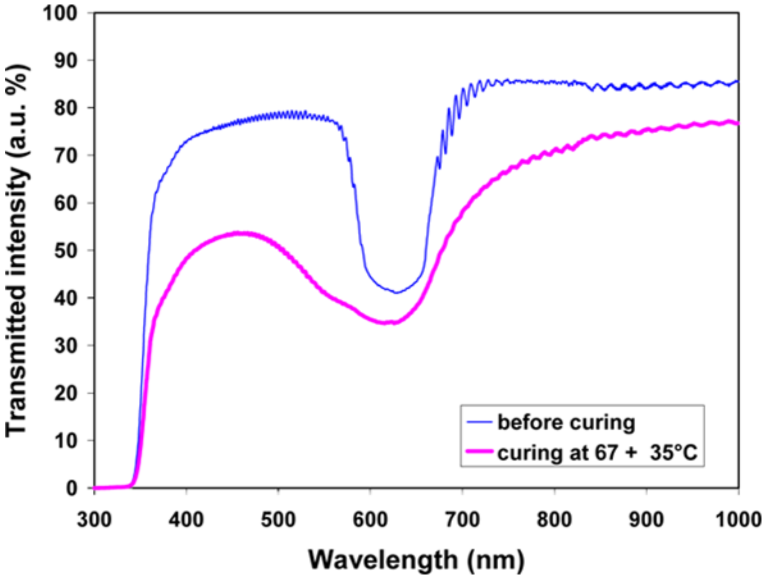

FIGURE 4 Transmitted light intensity of cells as a function of wavelength before and after curing at 67 and then 35°C. (See COLOR PLATE XXXIV)

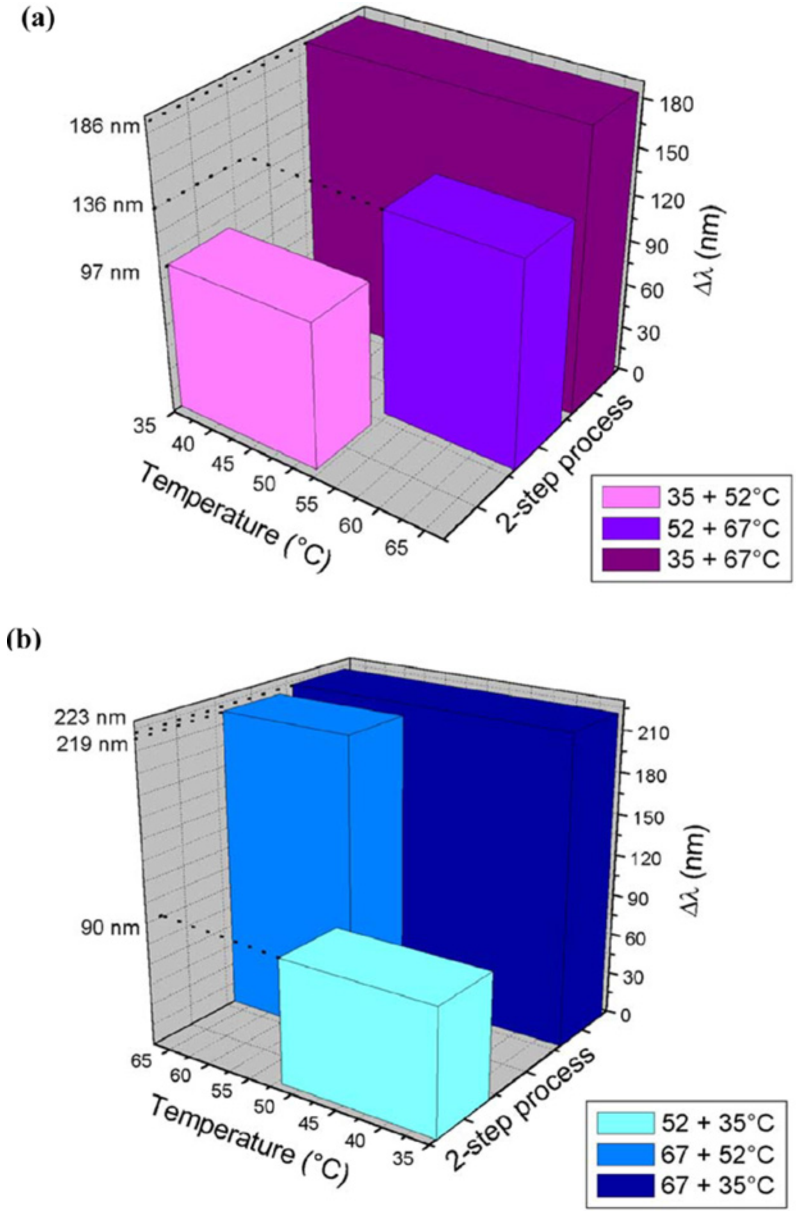

FIGURE 5 Reflection bandwidth $\Delta\lambda$ for different 2-step thermal processes when the curing occurred: (a) from the low to the high temperature or (b) from the high to the low temperature. (See COLOR PLATE XXXV)

occurs from high to low temperature. Let us note that very similar $\Delta\lambda$ are provided by the sequences 67 & 52°C and 67 & 35°C (respectively 219 and 223 nm).

III.4. Electro-optical Properties

The switchability properties of PSCLCs were investigated. In the case of a curing at 67°C, Figure 6 shows the variation of transmitted intensity with the wavelength at different operating voltages.

A set of curves which are typical of different modes is displayed. We distinguish five periods in the evolution of optical behaviour during a voltage increase. They correspond to different cell states:

- a broadened reflective state above 0 V and until 13 V: when the peaks are very similar to the peak at zero voltage;
- an association of reflective and scattering states from 15 to 21 V: the peak is progressively collapsing and the mean level of transmitted light is vanishing;
- a pure scattering state between 23 and 40 V: the cell has a milky aspect;
- a field-induced transition from scattering to transparent state from 50 to 100 V: the cell becomes more and more clear;
- the transparency is obtained from 120 V.

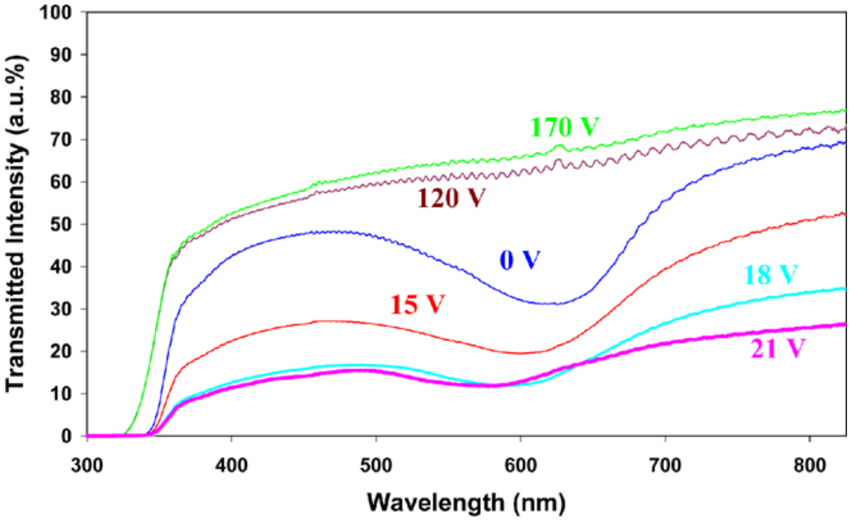

FIGURE 6 Transmitted light intensity of PSCLC cured at 67°C as a function of wavelength for different voltage values. (See COLOR PLATE XXXVI)

As in PSCLCs with narrow reflection bands, the light scattering is due to a focal conic texture exhibiting polydomains [9]. This is the result of a competition between LC molecules close to the polymer network which have a tendency to contribute to a stable planar reflecting texture and the electric field effect which is to destroy this order by untwisting the helix. Finally and for the higher voltages, the cell becomes transparent when the structure is untwisted and the free LC molecules are perpendicular to the electrodes.

IV. DISCUSSION AND CONCLUSION

PSCLCs have been elaborated by combining the UV-curing with a thermally-induced pitch variation. Different thermal processes were studied when the curing occurred at one or two temperatures. In the visible spectrum and with these novel experimental conditions-that we have labelled as out-of-equilibrium conditions – $\Delta\lambda$ is easily tunable by the choice of thermal process and can even be broadened by several orders of magnitude. In the same time the band position inside the spectrum is kept rather constant ($\bar{\lambda}$ is not significantly shifted). These preliminary results display $\Delta\lambda$ greater than 220 nm for a peak centred around 620–630 nm, which means that $\Delta\lambda$ is multiplied by a factor close to 2.6. The evolution of optical properties in relationship with other thermal processes (n-step process or a continuous thermal ramp with different ramp times) are under investigation and will be presented in a forthcoming paper. The PSCLCs are switchable: broadened reflective, scattering and transparent states are the main available modes when a cell is subjected to an increasing voltage.

In a previous work [10], we investigated a UV-curing associated to a thermally-induced pitch variation in the case of a CLC polymer-LMMCLC composite when the concentration in crosslinked polymer is high, *i.e.* 80 wt.%. We showed that the part of UV-curing is likely to keep memory of the pitch variation history during the thermal process. As brought to the fore by TEM investigations of a cross-section exhibiting the fingerprint texture, the broadening of the reflection band was correlated to a helical structure with a pitch gradient. Here, the experimental conditions are very different: the polymer concentration is very weak and if the network plays like a role of keeping in memory the pitch variation, these effects have to be transferred into the volume of LMMLC; the present work evidences that such a minor concentration in polymer is sufficient to induce a broadening of the reflection peak. Up to now, TEM investigations of the fine structure of polymer network remain difficult due to the fragility of the porous network.

How the network could induce a broadening of the reflection band for the whole composite material?

Firstly, we are not in a position to discuss the influence of the temperature variation during the UV-curing on parameters intrinsic to the crosslinking photoreaction such as the crosslinking rate which contributes to the three-dimensional nature of the network. Secondly and to give food for thought, we could discuss the role of Δn and p(z) on $\Delta\lambda$; p(z) represents the pitch variation where z denotes the distance from the UV-exposed surface into the film. We have not investigated the variation of Δn: *(i)* with the temperature; *(ii)* before and after UV-curing. However, on the former point and from previous studies in conventional LMMCLCs [11 and references therein] and PSCLCs [12], we expect a decrease of refractive indices when the temperature is increased from the room cholesteric temperature until the isotropization point. If the network contributes 'to memorize' these variations, and due to the fact that the processes from high to low temperature are the more suitable conditions to increase $\Delta\lambda$, the evolution of Δn with temperature would play against larger $\Delta\lambda$. On the latter case (Δn changes after curing), it has been shown in PSCLCs that the extraordinary refractive index of the material increased upon polymerization [12]. This increase was attributed to the increase in the order parameter of the LC as a result of the increased clearing point upon polymerization. However, this modest change in birefringence is not enough to explain the increase in $\Delta\lambda$. Therefore, a larger $\Delta\lambda$ upon out-of-equilibrium curing conditions, could be associated with the presence of a pitch distribution p(z) within the gel and perhaps a pitch gradient as evidenced by scanning or transmission electron microscopy in different polymeric [10,13] and glassy [14,15] materials; effectively, we know that the blend pitch increases with the temperature (Fig. 2) and that broadened bandwidthes were obtained when the more important temperatures were included in the curing process.

When the PSLC comes back to the ambient temperature after curing, two different populations of LMMLC molecules experiment the phase transition [16]; one population behaves like the bulky LC and recovers the helical structure stable at room temperature whereas the other population is strongly bound to the network and adopts a structure which is very dependent on the non-reversible orientation of macromolecular network. In the present case, this fraction of bound LC molecules could be sufficient to introduce into the optical properties some reminiscence of the pitch variation which led to broadened bandwidthes under peculiar thermal processes. Furthermore, in the case of a two-step process, the phenomenon of broadening depends on the order of the steps inside the sequence which will not be discussed here.

To broaden the light reflection band in CLCs is relevant for fundamental aspects as well as switchable displays like white-or-black polarizer-free flat panels or smart windows to control the solar light spectrum.

REFERENCES

[1] Dunmur, D. & Toriyama, K. (1999). In: *Physical Properties of Liquid Crystals*, Demus, D., Goodby, J., Gray, G. W., Spiess, H. -W., & Vill, V. (Eds.), Wiley-VCH: Weinheim, 124–128.

[2] In a Grandjean planar texture, the helix axis is perpendicular to the observation plane.

[3] $\bar{n}$ is the average of the ordinary (n_o) and extraordinary (n_e) refractive indices of the locally uniaxial structure: $\bar{n} = (n_o + n_e)/2$.

[4] $\Delta n = n_e - n_o$.

[5] For a recent review: Dierking, I., (2000). *Adv. Mater., 12*, 167.

[6] (1996). In: *Liquid Crystals in Complex Geometries*, Crawford, G. P. & Zumer, S. (Eds.)
  (a) D.-K., Yang, Chien, L.-C., and Fung, Y. K. *Polymer-stabilized Cholesteric Textures*, 103–142;
  (b) Yuan, H. *Bistable Reflective Cholesteric Displays*, Taylor and Francis: London, 265–280.

[7] Kreuzer, F.-H., Andrejewski, D., Haas, W., Häberle, N., Riepl, G., & Spes, P. (1991). *Mol. Cryst. Liq. Cryst.*, *199*, 345.

[8] Cano, R. (1967) (1968). *Bull. Soc. Fr. Minér. Cryst., 90*, 333; *91*, 20.

[9] Yang, D.-K., Chien, L.-C., & Doane, J. W. (1992). *Appl. Phys. Lett., 60*, 3102.

[10] Lavernhe, A., Mitov, M., Binet, C., & Bourgerette, C. (2001). *Liq. Cryst., 28*, 803.

[11] Kelker, H. & Hatz, R. (1980). *Handbook of liquid crystals.*, Verlag Chemie: Weinheim, 330–332.

[12] Hikmet, R. A. M. & Kemperman, H. (1999). *Liq. Cryst., 26*, 1645.

[13] Broer, D. J., Lub J., & Mol, G. N. (1995). *Nature*, *378*, 467.

[14] Mitov, M., Boudet, A., & Sopéna, P. (1999). *Eur. Phys. J. B*, *8*, 327.

[15] Mitov, M., Binet, C., Boudet A., & Bourgerette, C. (2001). *Mol. Cryst. Liq. Cryst., 358*, 209.

[16] Hikmet, R. A. M. (1991). *Mol. Cryst. Liq. Cryst., 198*, 357.